Determination of the magnetic anisotropy axes of single-molecule magnets

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Simple methods are presented allowing the determination of the magnetic anisotropy axes of a crystal of a single-molecule magnet (SMM). These methods are used to determine an upper bound of the easy axis tilts in a standard $Mn_{12}-Ac$ crystal. The values obtained in the present study are significately smaller than those reported in recent high frequency electron paramagnetic resonance (HF-EPR) studies which suggest distributions of hard-axes tilts.

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Single-molecule magnets (SMMs) are among the smallest nanomagnets that exhibit magnetization hysteresis, a classical property of macroscopic magnets [1, 2, 3, 4, 5]. They straddle the interface between classical and quantum mechanical behavior because they also display quantum tunneling of magnetization [6, 7, 8, 9, 10, 11, 12, 13, 14] and quantum phase interference [15, 16]. These molecules comprise several magnetic ions, whose spins are coupled by strong exchange interactions to give a large effective spin. The molecules are regularly assembled within large crystals, with all the molecules often having the same orientation. Hence, macroscopic measurements can give direct access to single molecule properties.

An important tool to tune the quantum properties is the application of transverse fields. In particular, the tunnel splitting can be tuned by a transverse field via the S_xH_x and S_yH_y Zeeman terms of the spin Hamiltonian [15, 16]. Therefore, in order to study the tunnel dynamics in SMMs, a precise alignment of the field directions is necessary.

In this communication, we present three simple methods to align the magnetic field that we have used for all our published micro-SQUID and micro-Hall probe measurements. Applied to the standard $Mn_{12}-Ac$ SMM, these methods have allowed us to estimate an upper bound of the distribution of easy axes. We found values that are significately smaller than those of recent high frequency electron paramagnetic resonance (HF-EPR) studies [17, 18, 19] which suggest distributions of hard-axes tilts with widths of 1.7° and 1.3° for standard and deuterated $Mn_{12}-Ac$ single-molecule magnets. A distribution of internal transverse magnetic fields was also suggested for the $Mn_{12}-BrAc$ SMM with hard-axes tilts of 7.3° [20].

All measurements were performed using a 2D electron gas micro-Hall probe. The high sensitivity allows the study of single crystals of SMMs on the order of 10 to 500 μm. The sample of the present study was $20 \times 6 \times 5$ μm^3. The field can be applied in any direction by separately driving three orthogonal coils. In this study, the fields were rotated in a plane given by the $a-$ and $c-$axes of a single crystal of $Mn_{12}-Ac$. The crystal was attached to the Hall probe so that it measured mainly the magnetization along the $c-$axis of the crystal.

The first method to find the easy axis of magnetization consists in measuring hysteresis loops as a function of the angle of the applied field. Typical results for angles close to the easy axis of magnetization are presented in Fig. 1a showing faster relaxation for larger misalignment angles. This behavior can be understood by separating the applied field into two components, one parallel and the other transverse to the easy axis of magnetization. The transverse component increases in general the tunnel rate via the S_xH_x and S_yH_y Zeeman terms of the spin Hamiltonian. Only for special cases, a decrease of the tunnel rate can be observed that is due to quantum interference [15, 16]. The positions of the tunnel resonances are only slightly affected by a small misalignment angle [21]. This method is therefore not very sensitive.

A second, very similar method consists of measuring hysteresis loops as a function of angle of the applied field, but for angles close to the hard plane of magnetization. Typical results are given in Fig. 1b, showing that the hysteresis loop is nearly closed when the field is aligned transverse to the easy axis. This method is more sensitive than the first one, but is often not very convenient.

A third method is shown in Fig. 2. Let's call (x, y, z) the coordinate system of the magnetic anisotropy of a SMM where the easy axis of magnetization is along z. Another coordinate system (x', y', z') is rotated by two misalignment angles (θ, ϕ) with respect to (x, y, z). The purpose of the method is to find the misalignment angles. For the sake of simplicity, the following discussion is in two dimensions. A generalization to three dimensions is straightforward and is discussed below. The two reduced coordinate systems (x, z) and (x', z') are misaligned by θ (Fig. 2). The method consists of sweeping the applied field H along z' in the presence of a constant transverse field $H^{\rm tr}$ applied along x'. The latter can be decomposed into $H_x^{\rm tr}$ and $H_z^{\rm tr}$ along x and z, respectively (Fig. 2).

$H_x^{\rm tr}$ modifies the tunnel rates of the spin system whereas $H_z^{\rm tr}$ shifts all resonance positions by the quantity

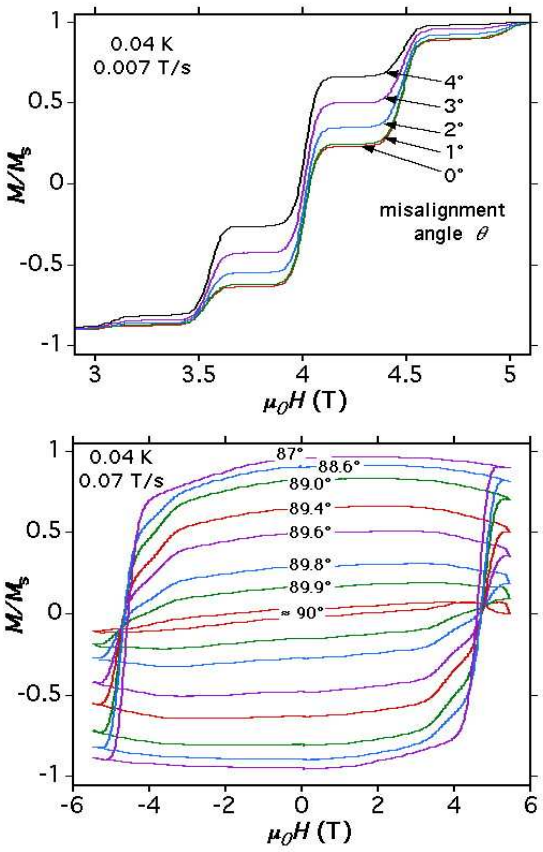

FIG. 1: (Online color) (a) Positive part of the hysteresis loop of a single crystal of $Mn_{12}-Ac$ for several misalignment angles. The magnetization M along the $c-$axis of the crystal is normalized by its saturation value M_s. The steps are due to resonant tunneling between the spin ground state with the quantum number $m = -10$ and excited state $m = 4, 3, \ldots, 0$. No clear difference is observed between the misalignment angles of 0 and 1°. (b) Similar hysteresis loops but for angles close to the hard plane (along the $a-$ axis of the crystal).

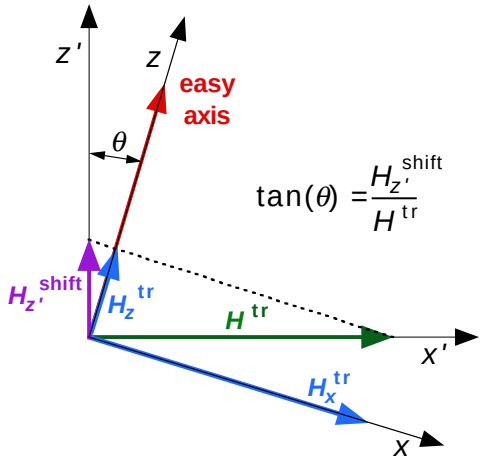

FIG. 2: (Online color) Scheme of the coordinate system (x, z) of the magnetic anisotropy of a SMM where the easy axis of magnetization is along z and a coordinate system (x', z'). The latter is rotated by a misalignment angles θ with respect to (x, z). The applied field H is swept along z' in the presence of a constant transverse field $H^{\rm tr}$ applied along x'. The latter can be decomposed into $H_x^{\rm tr}$ and $H_z^{\rm tr}$ terms along x and z, respectively (Fig. 2)

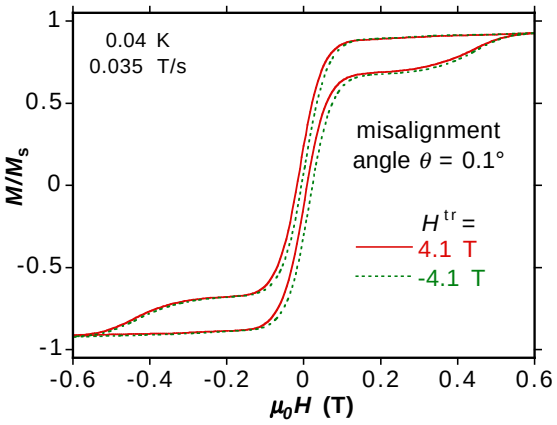

FIG. 3: (Online color) Normalized magnetization along the $c-$axis of the crystal versus a field applied at a misalignment angle $\theta = 0.1°$. A constant transverse field $H_{\rm tr} = \pm 4.1$ T is applied leading to clear field shifts $H_{z'}^{\rm shift} = H^{\rm tr}\tan(\theta) \approx$ O.OO7 T (Fig. 2) of the zero field resonance.

$H_{z'}^{\rm shift}$ along z' (Fig. 2):

$$H_{z'}^{\rm shift} = H^{\rm tr}\tan(\theta). \qquad (1)$$

Fig. 3 exhibits a typical measurement for $Mn_{12}-Ac$ for a misalignment angle of $\theta = 0.1°$ and $H^{\rm tr} = \pm 4.1$ T leading to $H_{z'}^{\rm shift} \approx \pm 0.007$ T. The latter can be measured easily, thereby allowing a field alignment much better than 0.1°.

In order to generalize the above method to a three dimensional alignment, it is convenient to choose two orthogonal planes. Firstly, the projection of the easy axis into one plane is measured. Then, the orthogonal plane is rotated so that it contains the easy axis projection. Finally, it is sufficiant to apply again the above method in this orthogonal plane in order to find the easy axis. The final result can be checked by sweeping the field along the easy axis in the presence of a constant transverse field. No net shifts of the resonance fields should be observed when comparing both parts of the hysteresis loops.

It is also important to note that the above method works in the thermally activated regime and even above the blocking temperature. In particular, only small transverse fields are needed at higher temperatures. For easy plane anisotropies and more complex anisotropies, analogues versions can be figured out easily.

We use here our methods to determine an upper bound of the easy axis tilts in a standard $Mn_{12}-Ac$ crystal.

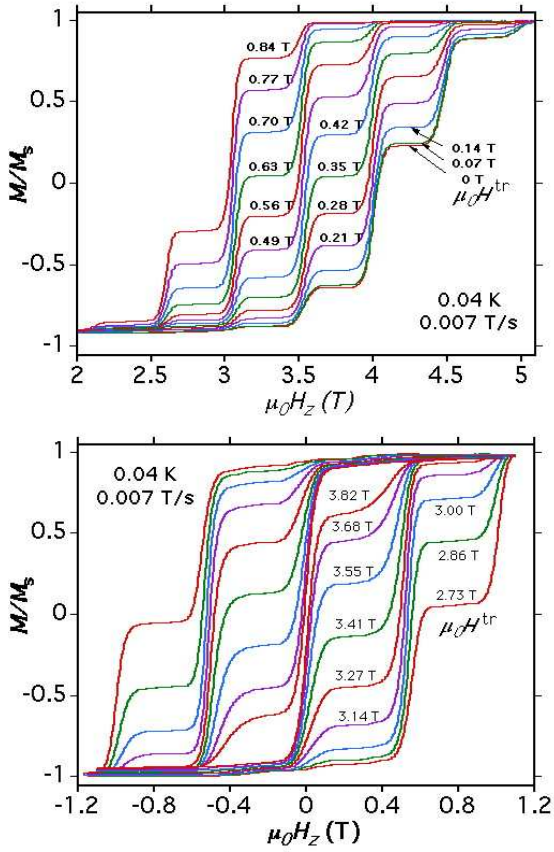

FIG. 4: (Online color) (a and b) Normalized magnetization along the $c-$axis of the crystal versus applied field along the $c-$axis for several constant transverse fields $H_{\rm tr}$. Although the transverse fields increase the tunnel rates, no significant broadening of the resonance fields is observed.

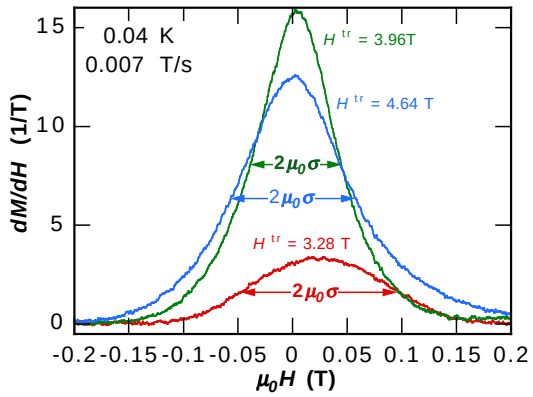

FIG. 5: (Online color) Derivative dM/dH of three hysteresis curves at the zero field resonance for a field sweep from negative to positive fields. The definition of the width σ at the half-width-at-half-maximum is shown.

We first align our fields with respect to the easy axis of $Mn_{12}-$Ac using the above methods. We measure then all tunnel transitions as a function of transverse field (Fig. 4) and study their widths σ. Fig. 5 presents the first derivative of the magnetization dM/dH for the zero field resonance for several transverse fields. We defined the resonance width σ as the half-width-at-half-maximum, in accordance with Ref. [17, 18, 19]. Fig. 6 presents σ as a function of a transverse field showing a minimum of the width at about 4 T. Recent HF-EPR studies [17, 18, 19] suggested that there are distributions of hard-axes tilts with widths of 1.7° and 1.3° for standard and deuterated $Mn_{12}-$Ac, respectively. Fig. 6 shows the expected width of the zero field resonance supposing that it is only due to the distribution of hard-axes tilts. Our results suggest an upper bound of 0.5°. The actual hard-axes tilts might be much smaller because we expect a dipolar broadening of the resonance lines of about 0.03 T. In addition, higher order tunneling transitions induced by dipolar and small superexchange interactions might further broaden the resonance transition [22]. We therefore believe that the hard-axes tilts should not exceed about 0.2°.

This result is confirmed by the second method. An upper bound for the hard-axis tilts is given by the angle needed to get a hysteresis loop that reaches $|M/M_{\rm s}| = 0.5$. We find $\theta = 89.6°$ (Fig. 1b), that is an upper bound of 0.4° for the hard-axis tilts. The actual value might be much smaller because we neglect here multi-body tunnel effects [22] that should be rather strong due to the high transverse fields.

We also applied our methods to the $Mn_{12}-$BrAc SMM and could not confirm the hard-axes tilts of 7.3° suggested by del Barco et al. [20]. Our results showed that the hard-axes tilts in $Mn_{12}-$BrAc might be even smaller than in $Mn_{12}-$Ac.

Finally, we speculate about the origin of the line widths observed in the EPR studies [17, 18, 19]. We suggest that the observed fine structures are due to the presence of fast relaxing species [31] having a smaller magnetic anisotropy and are tilted with respect to the $c-$axis by about 10° [23]. These species are coupled via dipolar interactions to the normal ones leading to multi-body effects (cross relaxations) [22] that might broaden the lines. Such an interpretation is supported by the fact that $Mn_{12}-$BrAc does not show anormalous EPR line width broadening [32] because it hardly has fast relaxing species.

In conclusion, we have presented three methods that allow the determination of the magnetic anisotropy axes of a crystal of a single-molecule magnet (SMM). The precise field alignments are necessary when studying quantitatively resonant tunneling of magnetizations in spin systems like SMMs.

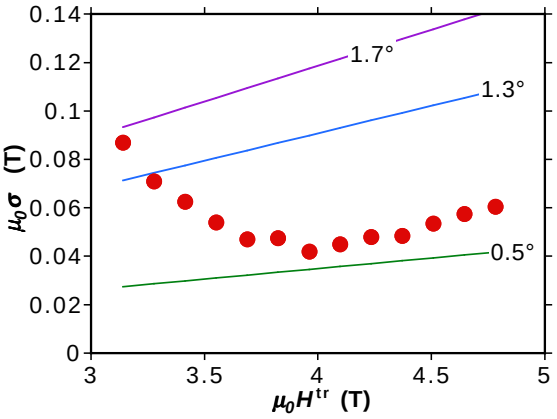

FIG. 6: (Online color) Half-width-at-half-maximum σ versus transverse field for the zero field resonance.

[1] G. Christou, D. Gatteschi, D.N. Hendrickson, and R. Sessoli, MRS Bulletin **25**, 66 (2000).

[2] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **115**, 1804 (1993).

[3] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature **365**, 141 (1993).

[4] S. M. J. Aubin and *et al.*, J. Am. Chem. Soc. **118**, 7746 (1996).

[5] C. Boskovic and et al., J. Am. Chem. Soc. **124**, 3725 (2002).

[6] M.A. Novak and R. Sessoli, in *Quantum Tunneling of Magnetization-QTM'94*, Vol. 301 of *NATO ASI Series E: Applied Sciences*, edited by L. Gunther and B. Barbara (Kluwer Academic Publishers, London, 1995), pp. 171–188.

[7] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[8] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).

[9] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).

[10] S. Hill, J.A.A.J. Perenboom, N.S. Dalal, T. Hathaway, T. Stalcup, and J.S. Brooks, Phys. Rev. Lett. **80**, 2453 (1998).

[11] S. M. J. Aubin, N. R. Dilley, M. B. Wemple, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **120**, 839 (1998).

[12] L. Bokacheva, A.D. Kent, and M.A. Walters, Phys. Rev. Lett. **85**, 4803 (2000).

[13] M. Soler, W. Wernsdorfer, K. Folting, M. Pink, and G. Christou, J. Am. Chem. Soc. 2156 (2004).

[14] A.J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K.A. Abboud, and G. Christou, Angew. Chem. Int. Ed. Engl. **43**, 2117 (2004).

[15] A. Garg, EuroPhys. Lett. **22**, 205 (1993).

[16] W.Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).

[17] S. Hill, R. S. Edwards, S. I. Jones, N. S. Dalal, and J. M. North, Phys. Rev. Lett. **90**, 217204 (2003).

[18] S. Hill, S. Takahashi, R. S. Edwards, J. M. North, and N. S. Dalal, cond-mat/0401515 .

[19] E. del Barco, A. D. Kent, S. Hill, J. M. North, N. S. Dalal, E. M. Rumberger, D. N. Hendrickson, N. Chakov, and G. Christou, cond-mat/0404390 .

[20] E. del Barco, A. D. Kent, N. E. Chakov, L. N. Zakharov, A. L. Rheingold, D. N. Hendrickson, and G. Christou, Phys. Rev. B **69**, 20411 (2004).

[21] The position of the resonances should increase roughly by the factor of $\cos(\theta)^{-1} \approx 1$ for small angles θ.

[22] W. Wernsdorfer, S. Bhaduri, R. Tiron, D. N. Hendrickson, and G. Christou, Phys. Rev. Lett. **89**, 197201 (2002).

[23] W. Wernsdorfer, R. Sessoli, and D. Gatteschi, EuroPhys. Lett. **47**, 254 (1999).

[24] D. Ruiz, Z. Sun, B. Albela, K. Folting, J. Ribas, G. Christou, and D. N. Hendrickson, Angew. Chem. Int. Ed. Engl. **37**, 300 (1998).

[25] Z. Sun, D. Ruiz, E. Rumberger, C. D. Incarvito, K. Folting, A. L. Rheingold, G. Christou, and D. N. Hendrickson, Inorg. Chem. **37**, 4758 (1998).

[26] Z. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, B. Maple, G. Christou, and D. N. Hendrickson, Chem. Commun. 1973 (1999).

[27] S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Rumberger, I. A. Guzei, K. Folting, P. K. Gantzel, A. L. Rheingold, G. Christou, and D. N. Hendrickson, Inorg. Chem. **40**, 2127 (2001).

[28] S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Rumberger, I. A. Guzei, K. Folting, P. K. Gantzel, A. L. Rheingold, G. Christou, and D. N. Hendrickson, Polyhedron **20**, 1139 (2001).

[29] M. Soler, W. Wernsdorfer, Z. Sun, D. Ruiz, J. C. Huffman, D. N. Hendrickson, and G. Christou, Polyhedron **22**, 1783 (2003).

[30] M. Soler, W. Wernsdorfer, Z. Sun, J. C. Huffman, D. N. Hendrickson, and G. Christou, Chem. Commun. 2672 (2003).

[31] Several authors have pointed out that in the Mn_{12} carboxylate family different isomeric forms give rise to different relaxation rates. This was first observed in Mn_{12}-ac [11, 24, 25, 26] and has been studied in detail [27, 28, 29, 30]. We found that a minor species of Mn_{12}-ac [23], randomly distributed in the crystal, exhibits a faster relaxation rate which becomes temperature independent below 0.3 K.

[32] K. Petukhov, S. Hill, N. E. Chakov, G. Christou, and K. Abboud, cond-mat/0403435.